RECYCLING COMMINGLED PLASTICS VIA SELECTIVE DISSOLUTION

BY

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INTRODUCTION

Plastics are an increasingly large component of household waste and offer great potential for resource and energy recovery through recycle. The typical household waste would be primarily composed of the following plastics: polyvinyl chloride (PVC), polystyrene (PS), low density polyethylene (LDPE), high density (HDPE), polyethylene polypropylene (PP), and polyethylene terephthatate (PET). Although plastics recycling will be mandated due to its limited resource nature and solid waste disposal problems, the main driving force for recycling will be economics. Plastics offer one of the truly recyclable materials of our age. We should not limit the end use of recycled plastics to low end markets which offer limited potential for economic gain through recycling.

Most pairs of polymers are incompatible and form two phases upon mechanical mixing. This incompatibility typically leads to poor physical properties unless one of the components is microdispersed in the other. To this end incentives exist to separate waste plastic streams into pure polymers or at least render innocuous certain components that may lead to poor physical properties. These polymers are in part separable from the mixed waste stream through bottle recycling programs and hand sorting. These methods tend not to be economical and problems remain even when these streams are separated from metals, cellulose, and other wastes. The major difficulty is that the plastics themselves are mixtures. This problem is of an increasing complexity with the advent of multi-layered containers.

OVERVIEW OF PROCESS

The same thermodynamic differences that cause incompatibility provide an opportunity to separate the components of a mixed plastic waste stream. In principle, a commingled plastic stream can be separated into pure components by selective dissolution followed by low solids flash devolatilization and compositional quenching. Figure 1. illustrates the basic flow diagram of the polymer reclamation process. Our process will require shredding of the commingled waste stream, which will probably be preformed at the collection site to reduce transportation costs. We have assumed collection and shredding to be outside the battery limits of our operation.

The commingled polymers will be separated using a controlled sequence of solvents and solvation temperatures. Dissolution is fast at low polymer concentrations, say 10% by weight or less. At these low concentrations, the viscosity will also be low, making filtration feasible. The filtration step will be used to remove insoluble contaminates such as metals, glass, cellulose and some pigments. Since the polymers are in solution this affords an opportune time to add stabilizers and impact modifiers to obtain a value added product.

EXPERIMENTAL PROCEDURE

Figure 2 illustrates the apparatus used for Rensselaer's polymer reclamation project. The apparatus is the combination of two technologies, selective dissolution and low solids flash devolatilization. Our current reclamation project is a natural evolution from work focused on impact modification of polymers via flash devolatilization and compositional quenching. This is where two incompatible polymers are dissolved in a common solvent to form a homogeneous mixture. Phase separation occurs when the solvent is rapidly removed by flash devolatilization. The devolatilization step is fast and it plunges the residual, polymer/polymer/solvent mixture deep into a region of two phases. Phase separation occurs by spinodal decomposition and generates a microdispersion with a characteristic and small phase separation distance. If one of the phase volumes is small, a uniformly sized dispersion will result.

The selective dissolution apparatus is the first phase of our reclamation technology. The commingled plastic waste, typically 25 kg, is placed in the dissolution column with screen packs at both ends. A stirred vessel would be preferred but a column is a suitable substitution on this scale due to its ease of fabrication. A gear pump is used to circulate solvent, typically 20 liters, through the heat exchanger and dissolution column. dissolution is performed in the sequential batch mode. A unique temperature for a given solvent is used to selectively extract a single polymer group from the commingled stream. The polymer obtained from a single extraction is isolated via flash devolatilization. The recovered polymer is pelletized, while the recovered solvent is returned to the dissolution reservoir to extract the next polymer group at a higher temperature. It is this series of controlled temperature-solvent extractions facilitates the separation of individual polymers from a commingled waste stream.

The second phase, low solids flash devolatilization is a relatively simple process and readily scalable. The dissolution step is typically batch, but the flash devolatilization process is continuous thereafter. The polymer concentrations are typically 5-10% by weight. The feed solution is metered into a heat exchanger by a positive displacement pump. The pressure is maintained sufficiently high to ensure that no boiling occurs. The pressure is This pressure is regulated by a back-pressure or flash valve and is constrained at a minimum value, typically 10-40 atm. temperature upstream of the flash valve, typically 200-300°C, is one of the independent variables that governs the devolatilization The flash chamber pressure, typically 5-100 torr, is the other independent variable. Together they determine the polymer concentration after the flash, typically 60-95%, and the after flash temperature, typically 0-100°C. To a first approximation, the flash achieves vapor-liquid equilibrium.

EXPERIMENTAL RESULTS

Tetrahydrofuran (THF) was selected as our first trial due to the vast data base accumulated in prior solvent compositional quenching work. A commingled polymer sampled was prepared using equal volumes of virgin polymers from the major packaging groups : PVC, PS, PP, LDPE, HDPE, and PET. Figure 3 illustrates a split obtained using THF as the dissolution solvent. At 25°C using THF, we obtain a split containing commingled Polyvinyl chloride (PVC) and Polystyrene (PS). As an alternative, it has been determined that a previous extraction at 25°C with Dicloromethane will remove the PS and a subsequent extraction with THF at 25°C will remove the PVC. The second cut with THF at will extract the Low Density Polyethylene (LDPE) at 70°C. The third cut, consisted of commingled Polypropylene (PP) and High Density Polyethylene (HDPE) occurred at 160°C. The final cut was made at 190°C, which removed the Polyethylene terephthalate (PET). Using this synthetic waste stream, we have determined that separation efficiencies are very good, usually > 99%.

ECONOMICS

For our preliminary economic analysis, we will use THF as our dissolution solvent. THF will probably not be our solvent of choice, but represents a worst case scenario due to its high cost and relatively high volatility. The pressure required for the PET extraction at 190°c, will be 17 atm to prevent boiling. The high pressure will increase capital equipment costs. Due to economic and environmental concerns, we will require the recovery of virtually all our solvent. To this end, the high volatility of THF will give an upper bound on recovery costs.

We estimate that a 50 million pound a year plant is required to operate cost effectively. We will assume that only electrical power will be consumed by this plant. Our assumed power costs are 4.5 cents per kilowatt hour. This figure would differ greatly depending on geographic location. Figure 4 illustrates the costs incurred when we pay 10 cents a pound for the commingled waste. The remaining raw material cost is for impact modifiers. A cost estimate of 25.9 cents a pound is achieved with no heat integration. Figure 5 illustrates the incorporation of heat integration and a zero raw material charge. Here we achieve a processing cost of 12.2 cents a pound.

CONCLUSIONS

Although this project is in its infancy, initial results are very promising. When fully developed, this technology may be one of the key answers to polymer reclamation. Using THF we have demonstrated a four way split of the six major packaging plastics. Preliminary indications are that solvents exist to separate cleanly all six major plastic groups. With greater than 99% separation efficiencies, compositional quenching will microdisperse the minor components and render them innocuous. It is believed that the split which contains the PP and HDPE will exhibit good physical properties. We do not expect the same for the PVC and PS split. If THF is to be used as the dissolution solvent, a second solvent, eg. methylene chloride, can be used to extract the PS prior to the room temperature THF extraction.

Preliminary economics demonstrate an expected processing cost of 12 to 26 cents a pound. Individual assumptions and cost estimates can be argued, but we believe them to be within standard estimation errors. The use of alternate solvents should also reduce the cost of processing. The added product value our technology attains combined with the ability to use existing markets, makes this is an economically attractive process.

Efforts are currently under way to determine the dissolution characteristics for a true commingled waste stream. Due to the variation in molecular weight, branching, and copolymers among manufacturers, we anticipate that separation efficiencies will be lower for actual waste steams. We expect that compositional quenching will overcome the potential problems which may result from the reduced efficiencies. Problems which also may occur due to insoluble contaminants and soluble contaminants will also be addressed. The next stage is the design of a nominal 100 pound per hour pilot plant.

NOMENCLATURE

HDPE High density polyethylene

LDPE Low density polyethylene

PET Polyethylene terephthalate

PP Polypropylene

PS Polystyrene

PVC Polyvinyl chloride

THF Tetrahydrofuran

ACKNOWLEDGEMENTS

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FIGURE 1: PROCESS FLOW CHART

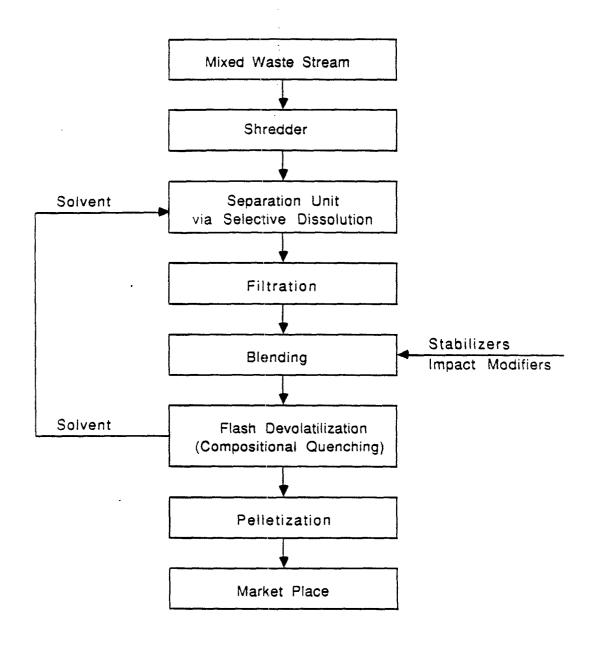


Figure 2 - Polymer Reclamation Apparatus

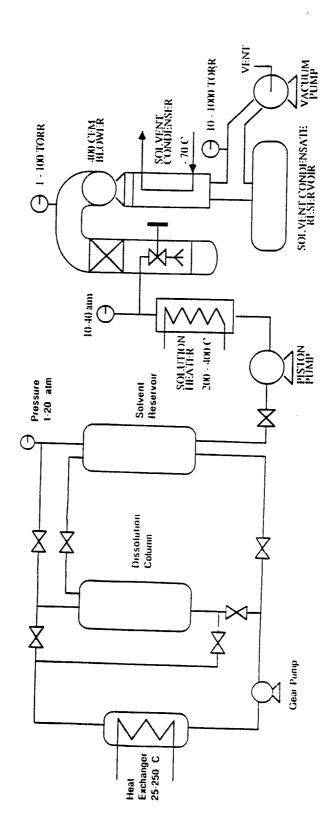


FIGURE 3: SELECTIVE DISSOLUTION USING TETRAHYDROFURAN

First Cut: Room Temperature

PVC

PS >99%

Second Cut: 70°C

LDPE >99%

Third Cut: 160°C

PP >99%

HDPE >99%

Fourth Cut: 190°C

PET >99%

[•]Experiments were conducted with virgin polymers.
•Extraction percents were measured using a gravimetric technique.

Figure 4 - Manufacturing Cost Summary

Job Title Polymer Rec	laimation Project	Cost Index Type Cost Index Value	CE Index 346
Fixed Capital	\$5,532,848		
Working Capital	\$1,106,570		
Total Capital Investment	\$6,639,418		
	\$/Year	\$/1 b	
Manufacturing Expenses Direct			
Raw Materials	36,245,110	0.1183	
Solvents	\$151,652	0.0029	
Operating Labor	\$768,600	0.0146	
Supervisory & Clerical Labor	\$153,720	0.0148	
Utilities	3133,720	0 0023	
Electric Power	31,504,947	0.0285	
Maintenance & Repair	\$640.885	0.0121	
Operating Supplies	\$128,177	0.0024	
Laboratory Charges	\$153.720	·	
Patents & Royalties	\$437,105	0.0029	
raterits a ricyanies	3437,103	0.0083	
Total Direct Expenses	\$10,183.915	0.1929	
Indirect			
Overhead	\$1,094,243	0.0207	
Local Taxes	\$110.657	0.0021	
Insurance	\$55.328		
	333,326	0.0010	
Total Indirect Expenses	\$1,260.229	0.0239	
Total Manufacturing Expense	\$11,444,144	0.2168	
Depreciation	\$553.285	0.0105	
General Expenses			
Administrative Costs	\$273,561	0.0052	
Distribution & Selling Costs	\$728.653	0.0032	
Reasearch & Developement	\$364,401		
	3304,401	0.0069	
Total General Expense	\$1,366,615	0.0259	
Total Expense	\$13,364,044	0.2531	

Figure 5 - Manufacturing Cost Summary Alt. Case

Job Title Polyme	r Reclaimation Project	Cost Index Type Cost Index Value	CE index 346
Fixed Capital	\$5,532,848		
Working Capital	\$1,106,570		
Total Capital Investme	ent \$6,639,418		
	\$/Year	\$/1b	
Manufacturing Expenses			
Direct			•
Raw Materials	SO	0.0000	
Solvents	\$151,652	0.0029	
Operating Labor	\$768,600	0.0148	
Supervisory & Clerical Labor Utilities	\$153,720	0.0030	
Electric Power	\$743,322	0.0143	
Maintenance & Repair	\$640,885	0.0123	
Operating Supplies	\$128.177	0.0025	
Laboratory Charges	\$153,720	0.0030	
Patents & Royalties	\$437,105	0.0084	
Total Direct Expenses	\$3,177,180	0.0610	
Indirect			
Overhead	\$1,094,243	0.0210	
Local Taxes	\$110,657	0.0021	
Insurance	\$55,328	0.0011	
Total Indirect Expense	\$ \$1,260,229	0.0242	
Total Manufacturing Ex	xpense \$4,437,409	0.0853	
Depreciation	\$553,285	0.0106	
General Expenses			
Administrative Costs	\$273,561	0.0053	
Distribution & Selling Costs	\$728,653	0.0140	
Reasearch & Developement	\$364,401	0.0070	
Total General Expense	\$1,366,615	0.0263	
Total Expense	\$6,357,309	0.1221	

TECHNOLOGY

Chemists Seek Ways to Recycle Plastics Before Movement to Ban Products Grows

By Amal Kumar Naj

Staff Reporter of THE WALL STREET JOURNAL Chemists say they are on their way to solving a recycling riddle that will let consumers continue to use the plastic shopping bags, bottles, cups and other items to which they have become accustomed.

Right now, the inherent chemistry of plastics makes it impractical and uneconomical to melt such items into reusable scrap. As a result, an increasing number of communities, supermarkets and fastfood restaurants are banning the material altogether.

"At stake is the future of the plastics industry," says Darrell Morrow, the projects manager of a major recycling effort involving industry and government at Rutgers University. "We are convinced that we can reclaim plastics and find economical uses," he says.

But the task isn't easy, and researchers are trying a variety of approaches. The problem is that different plastic resins, because of their different molecular structures, are like oil and water—they don't mix. And most plastic products are made up of several different resins. A single beverage bottle, for example, contains at least three. Melted together, multiple resins form a dark mush of little economic value

Chemical companies have been experimenting with this brittle lump to make such prosaic items as bricks, lumber, fence posts, park benches and insulation. But such products, generally flammable and weak, have limited uses. "There's no doubt that ultimately we have to be able to separate the resins and recycle them to [high value] products," says Donald Genson, business director of solid waste management at **Dow Chemical** Co.

"My starting material is the black mush," says Bruce Nauman, a chemical engineer at Rensselaer Polytechnic Institute in Troy, N.Y. He says that he and several colleagues have been able to separate a mixture of six different polymers—used to make such different products as beverage bottles, oil containers, films, cups, packaging materials and labels—that account for more than 90% of plastic trash.

His technique involves dissolving the mixture in a solvent of xylene at different temperatures. Polystyrene, a packaging material, dissolves in the solvent at room temperature; the next polymer—low density polyethylene, used in plastic films—dissolves at 75 degrees Celsius; and the rest dissolve at temperatures that reach a high of 138 degrees Celsius for the polyvinyl chloride used in motor oil containers.

"It is a process that can get the polymers essentially in the form they left the factory," Mr. Nauman says. "This is the most innovative recycling technology in the world today."

But Rutgers's Mr. Morrow has more faith in the physical separation technique

being pursued at his university's Center for Plastic Recycling Research. "We have stayed away from the chemical process, because that won't be economical," he says.

Rutgers's approach calls for careful separation of different plastics at the consumer level—Coca-Cola bottles from Styrofoam cups, for instance—and further sorting at collection centers. Different resins are then separated using a mechanical process that takes advantage of differences in their gravity and electric charges. Elaborate filtering mechanisms further purify each resin. Sidney Rankin, another researcher on the project, says that two of the most widely used plastics that go into beverage bottles and milk containers "can be recycled as virgin resins."

Researchers at Dow and Du Pont Co. are trying an altogether different tack aimed at bypassing the need for separating resins. This approach is based on the fact that many new resins are created by manipulating the chemical structures of existing ones. The researchers are developing molecules that are attracted at one end to the molecule of one resin and at the other end to the molecule of another resin, thereby binding two incompatible resins into a plastic that may have useful properties for new applications.

No Details

The researchers decline to disclose details of the so-called compatiblizers, or binding agents. "At this stage of the game, we don't want to tip our hands to competitors," says Dow's Mr. Genson.

Under intense political pressure, almost all the major companies have plunged into recycling ventures. Last April. Du Pont formed a joint venture with Waste Management Inc., and last June seven polystyrene makers, including Dow. Amoco Corp. and Mobil Corp., formed a company to open recycling centers across the country to reclaim the material that goes into throwaway cups and fast-food containers.

But no matter how well the resins are separated and purified, researchers doubt that any recycled plastics will find their way back into food and beverage containers any time soon. They say the fear of oils, chemicals and metals contaminating the recycled material would make it hard to get Food and Drug Administration approval for such use.

Rutgers's Mr. Morrow says most uses will probably be in non-food areas. He says that **Procter & Gamble** Co. is currently evaluating containers made from recycled soft drink bottles to package a liquid detergent. Other major uses, he says, could be in automobiles.